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54 **Liquid crystal polyester resin composition.**

57 The present invention provides a liquid crystal polyester resin composition, which is manufactured at low cost and has favorable gas barrier properties and improved impact resistance, vibration-damping properties, thin-wall properties (mechanical properties of thin-wall molded articles), and film-forming properties, while maintaining excellent heat resistance and mechanical properties of a liquid crystal polyester. A liquid crystal polyester resin composition of the invention includes 55.0 through 99.9 percent by weight of a liquid crystal polyester as a component (A) and 0.1 through 45.0 percent by weight of an epoxy group-containing ethylene copolymer as a component (B), wherein the component (B) includes: (a) 50 through 96.5 percent by weight of an ethylene unit; (b) 0.5 through 30 percent by weight of an unsaturated glycidyl carboxylate unit or an unsaturated glycidyl ether unit; and (c) 3 through 40 percent by weight of an ethylenically unsaturated ester compound unit.

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The present invention relates to a liquid crystal polyester resin composition applicable to molded articles prepared by injection molding or extrusion molding.

Unlike crystalline polyesters such as polyethylene terephthalate and polybutylene terephthalate, a liquid crystal polyester consisting of rigid molecules does not become entangled even under the melting condition, but forms a polydomain in a liquid crystal state and has low shear properties to realize a remarkably high orientation of molecular chains towards the flow. The liquid crystal polyester is one example of thermotropic liquid crystal polymers. This specific behavior causes excellent melt flow properties and gives thin-wall molded articles of 0.2 through 0.5 mm in thickness having high strength and high rigidity. Molded articles of a liquid crystal polyester, on the other hand, have various disadvantages, including extremely large anisotropy and insufficient vibration-damping properties. The high molding temperature and high manufacturing cost of a liquid crystal polyester undesirably restrict its applications to various fields.

In the market, there has been a growing demand for an improved liquid crystal polyester resin composition, which is manufactured at low cost and realizes improved vibration-damping properties and anisotropy of molded articles while maintaining excellent heat resistance and mechanical properties of a liquid crystal polyester.

A resin composition disclosed in JAPANESE PATENT LAYING-OPEN GAZETTE No. S-56-115357 includes a melt processable polymer and an anisotropic melt processable polymer. The processabilities of a melt processable polymer have been enhanced by mixing an anisotropic melt processable polymer with the melt processable polymer. An example of such resin compositions is a mixture of polyphenylene ether and polystyrene blended with a liquid crystal polyester.

Another resin composition disclosed in JAPANESE PATENT LAYING-OPEN GAZETTE No. H-2-97555 is prepared by mixing a variety of polyarylene oxides with a liquid crystal polyester to improve the solder heat resistance.

Any conventional resin composition prepared by mixing a liquid crystal polyester of a high molding temperature with a non-crystalline polymer of a lower molding temperature, such as polyphenylene ether, results in poor appearance of molded articles due to pyrolysis of the resin mixture during the high-temperature molding while having the improved melt processability. Other drawbacks include insufficient heat resistance, mechanical properties, and impact resistance of the resulting composition.

Proposed resin compositions including a liquid crystal polyester and an aromatic polycarbonate, as disclosed in JAPANESE PATENT LAYING-OPEN GAZETTES No. S-57-40551 and No. H-2-102257, do not have sufficient heat resistance or mechanical properties.

Another known composition prepared by blending a liquid crystal polymer with epoxy rubber disclosed in the US Patent No. 5,216,073 also has insufficient heat resistance and mechanical properties.

Other proposed compositions prepared by mixing a thermoplastic resin with a liquid crystal polymer, as disclosed in JAPANESE PATENT LAYING-OPEN GAZETTES No. S-58-201850, No. H-1-121357, and No. H-1-193351, do not have favorable properties.

The object of the invention is to provide a liquid crystal polyester resin composition, which is manufactured at low cost and has favorable gas barrier properties and improved impact resistance, vibration-damping properties, thin-wall properties (mechanical properties of thin-wall molded articles), and film-forming properties, while maintaining excellent heat resistance and mechanical properties of a liquid crystal polyester.

The above and the other related objects are realized by a liquid crystal polyester resin composition including 55.0 through 99.9 percent by weight of a liquid crystal polyester as a component (A) and 0.1 through 45.0 percent by weight of an epoxy group-containing ethylene copolymer as a component (B). The component (B) specifically includes:

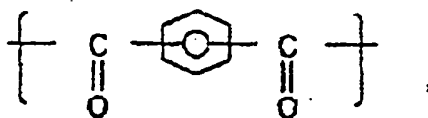
- (a) 50 through 96.5 percent by weight of an ethylene unit;
- (b) 0.5 through 30 percent by weight of an unsaturated glycidyl carboxylate unit or an unsaturated glycidyl ether unit; and
- (c) 3 through 40 percent by weight of an ethylenically unsaturated ester compound unit.

The liquid crystal polyester of component (A) may be obtained through a reaction of an aromatic dicarboxylic acid, an aromatic diol, and an aromatic hydroxycarboxylic acid or through a reaction of different aromatic hydroxycarboxylic acids.

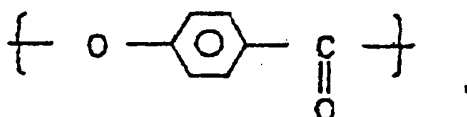
The liquid crystal polyester of component (A) may consist of repeat units given as Chemical Formulae 1 or Chemical Formulae 2 below:

## [Chemical Formulae 1]

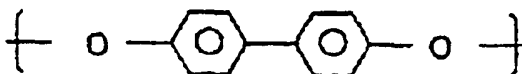
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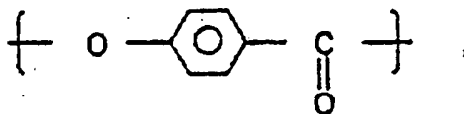
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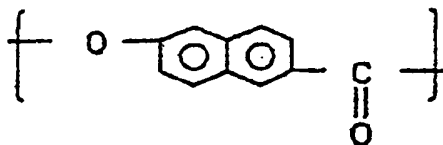
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## [Chemical Formulae 2]

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35 It is preferable that the epoxy group-containing ethylene copolymer of component (B) has a stiffness modulus in a range of 10 through 1,300 kg/cm<sup>2</sup>.

The liquid crystal polyester resin composition has a melt viscosity ratio (melt viscosity 2 / melt viscosity 1) of 0.1 through 0.7 being measured at a shear rate of either 100 sec<sup>-1</sup> or 1000 sec<sup>-1</sup>, said melt viscosity 1 being measured at a flow temperature and said melt viscosity 2 being measured at a temperature of 40 20 °C higher than said flow temperature.

The flow temperature initiates formation of an anisotropic melt phase and gives a melt viscosity of 48,000 poise when a resin heated at a rate of 4 °C/minute is extruded from a nozzle having an inner diameter of 1mm and length of 10 mm under a load of 100 Kgf/cm<sup>2</sup>.

45 It is preferable that the flow temperature of the liquid crystal polyester resin composition is higher than a flow temperature of the liquid crystal polyester of component (A).

The liquid crystal polyester of component (A) included in the liquid crystal polyester resin composition according to the invention is a thermotropic liquid crystal polymer. The liquid crystal polyester of component (A) may be obtained through one of the following reactions, which form an anisotropic melt at the temperature equal to or lower than 400 °C: .

- 50 (1) a reaction of an aromatic dicarboxylic acid, an aromatic diol, and an aromatic hydroxycarboxylic acid;  
 (2) a reaction of different aromatic hydroxycarboxylic acids;  
 (3) a reaction of an aromatic dicarboxylic acid and a nuclear substituted aromatic diol; and  
 (4) a reaction of an aromatic hydroxycarboxylic acid and a polyester, such as polyethylene terephthalate.

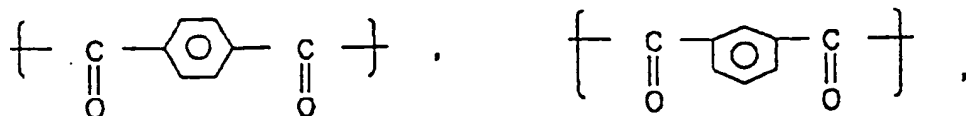
55 The aromatic dicarboxylic acid, the aromatic diol, and the aromatic hydroxycarboxylic acid may be replaced by ester derivatives thereof. Exemplified repeat units of the liquid crystal polyester are given below.

Repeat units originating from aromatic dicarboxylic acids:

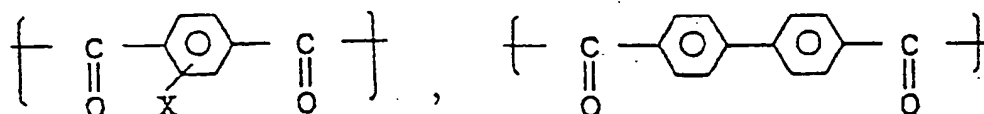
[Chemical Formulae 3]

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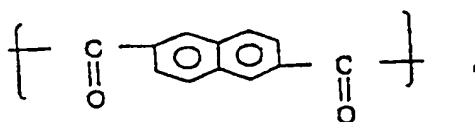
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where X denotes a halogen, alkyl, or aryl, whereby preferred halogen is e.g. Cl or Br, preferred alkyl is e.g. methyl or ethyl, and preferred aryl is e.g. phenyl.

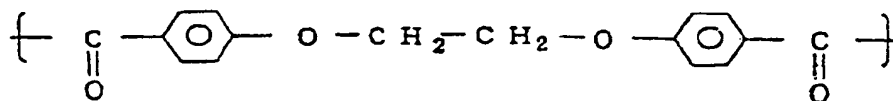
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[Chemical Formulae 4]

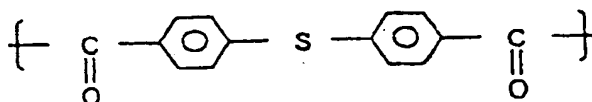
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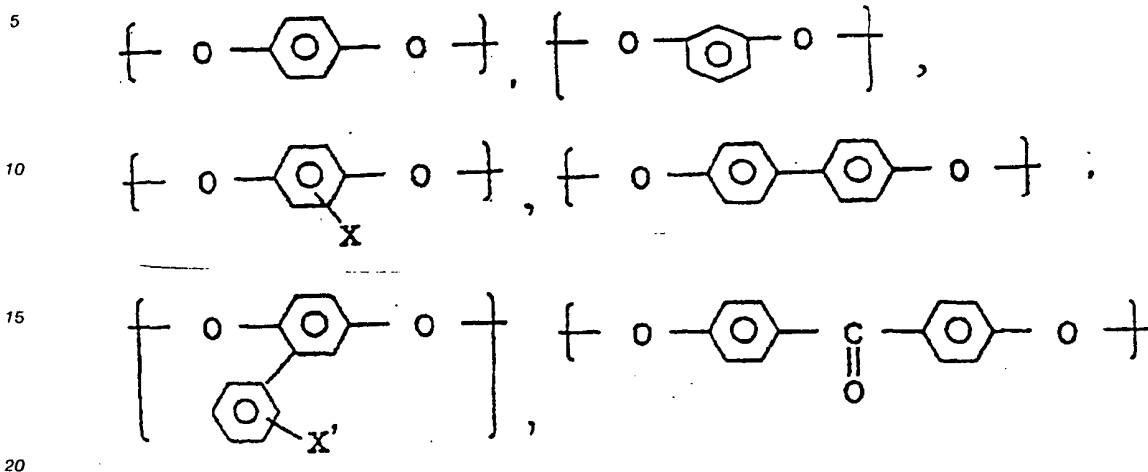
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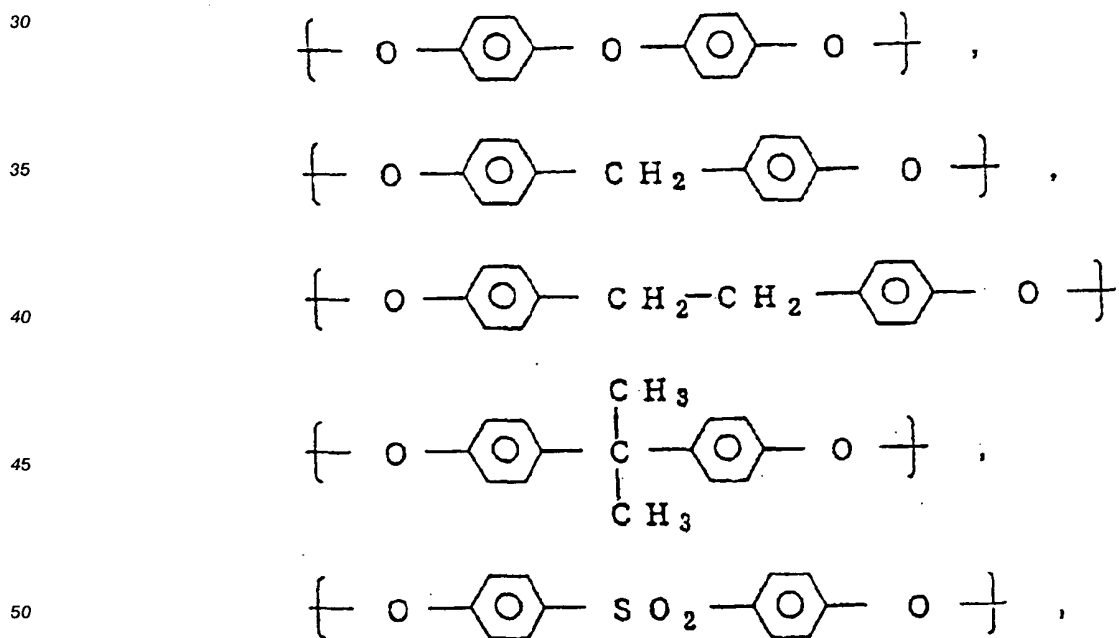
Repeat units originating from aromatic diols:

[Chemical Formulae 5]

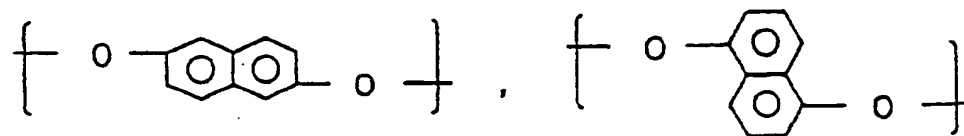
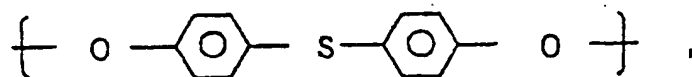


where X denotes a halogen, alkyl, or aryl; X' denotes a halogen or alkyl, whereby preferred halogen is e.g. Cl or Br, and preferred alkyl is e.g. methyl or ethyl.

[Chemical Formulae 6]

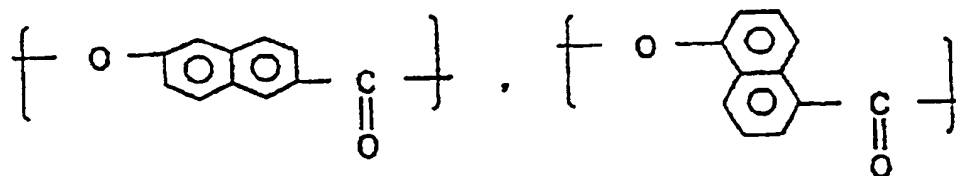
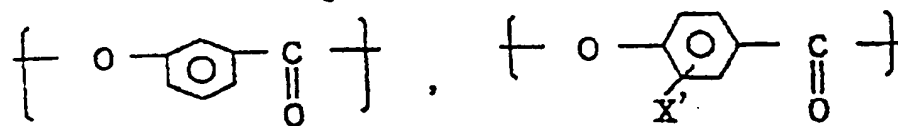
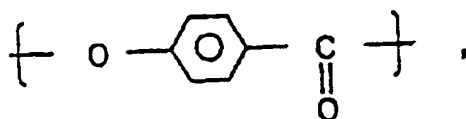


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Repeat units originating from aromatic hydroxycarboxylic acids:

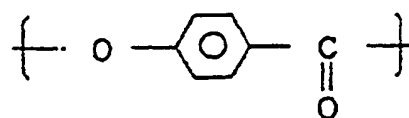
[Chemical Formulae 7]



where X' denotes a halogen or alkyl.

The liquid crystal polyester consisting of repeat units given as Chemical Formula 8 below has well-balanced heat resistance, mechanical properties and melt processabilities, and is preferably applied to the invention:

[Chemical Formula 8]

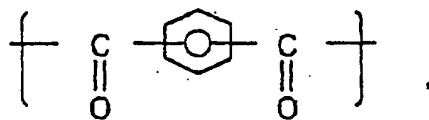


More concretely, the liquid crystal polyester preferably has one of the following combinations of repeat units (I) through (V):

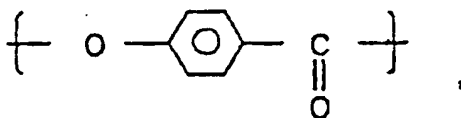
## [Chemical Formulae 9]

(I)

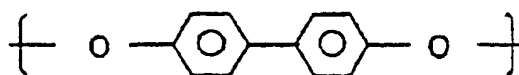
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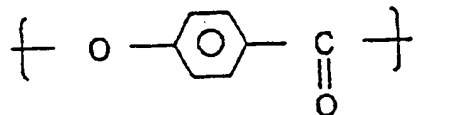


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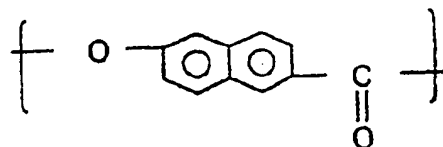
## [Chemical Formulae 10]

(II)

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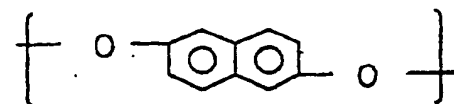
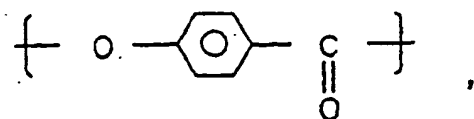
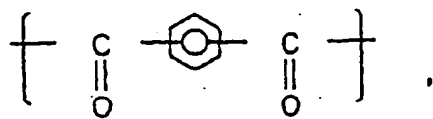
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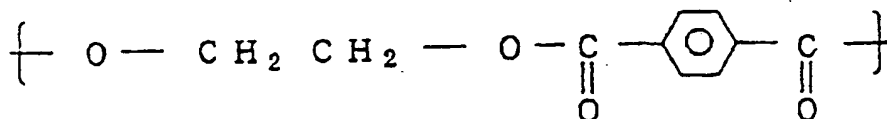
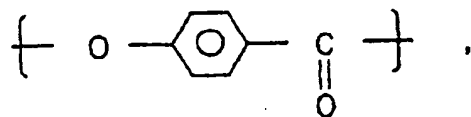
## [Chemical Formulae 11]

(III)



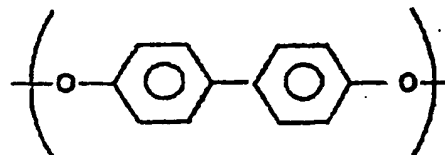
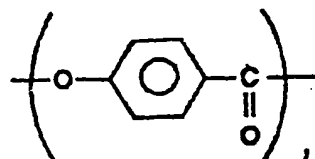
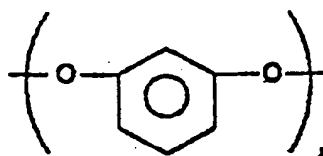
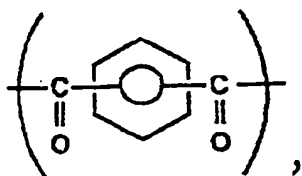
## [Chemical Formulae 12]

(IV)



## [Chemical Formulae 13]

(V)



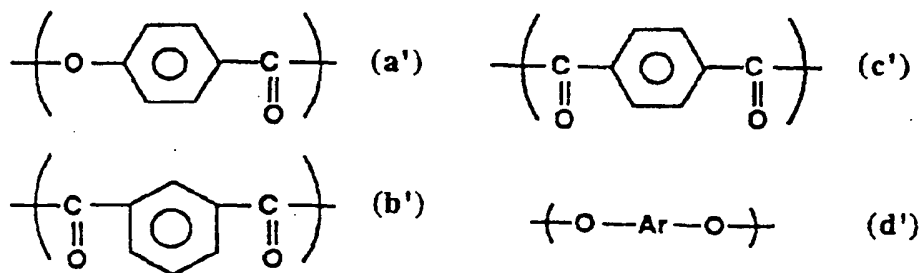
The liquid crystal polyesters (I), (II), (III), and (IV) are specified, for example, in JAPANESE PATENT PUBLICATION GAZETTES No. S-47-47870, No. S-63-3888, No. S-63-3891, and No. S-56-18016, respectively. The repeat unit combinations (I) and (II) are especially preferable among the above structures.

For application of the liquid crystal polyester resin composition according to the invention to fields with a requirement of high heat resistance, the liquid crystal polyester of component (A) preferably includes 30 through 80 percent of a repeat unit (a'), 0 through 10 percent of a repeat unit (b'), 0 through 25 percent of a



repeat unit (c'), and 10 through 35 percent of a repeat unit (d') in molar fractions.

[Chemical Formulae 14]



where Ar represents a divalent aromatic group, whereby preferred divalent aromatic groups are e.g. 1,4-phenylene and 4,4'-biphenylene.

The inherent viscosity ( $\eta_{inh}$ ) of the liquid crystal polyester applied to the invention is measured in the following manner: dissolving 0.1 g of the liquid crystal polyester in 10 cc of 2,3,5,6-tetrachlorophenol and measuring the inherent viscosity  $\eta_{inh}$  at 60 °C with an Ubbelohde viscometer.

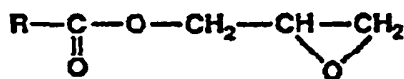
The inherent viscosity ( $\eta_{inh}$ ) of the liquid crystal polyester applied to the invention ranges from 1.0 to 8.0 or more specifically from 2.0 to 6.0. When the inherent viscosity  $\eta_{inh}$  of the liquid crystal polyester is out of the above range, the resin composition obtained has poor processabilities, mechanical properties, and heat resistance

The epoxy group-containing ethylene copolymer included as the component (B) in the liquid crystal polyester resin composition of the invention includes:

- (a) 50 through 96.5 percent by weight of an ethylene unit;
- (b) 0.5 through 30 percent by weight or more preferably 0.5 through 20 percent by weight of an unsaturated glycidyl carboxylate unit or an unsaturated glycidyl ether unit; and
- (c) 3 through 40 percent by weight of an ethylenically unsaturated ester compound unit.

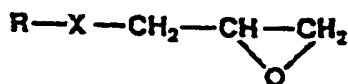
In the epoxy group-containing ethylene copolymer of component (B), compounds expressed as Chemical Formula 15 and Chemical Formula 16 yield the constituent (b), the unsaturated glycidyl carboxylate unit or the unsaturated glycidyl ether unit.

[Chemical Formula 15]



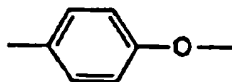
where R represents a hydrocarbon group having an unsaturated ethylene bond and containing 2 through 13 carbon atoms.

[Chemical Formula 16]



where R represents a hydrocarbon group having an unsaturated ethylene bond and containing 2 through 18 carbon atoms, and X denotes -CH<sub>2</sub>-O- or a group given below:

## [Chemical Formula 17]



5

Concrete examples include glycidyl acrylate, glycidyl methacrylate, glycidyl itaconate, allyl glycidyl ether, 2-methylallyl glycidyl ether, and styrene-p-glycidyl ether.

The epoxy group-containing ethylene copolymer of component (B) according to the invention is a terpolymer or another copolymer containing ethylene, unsaturated glycidyl carboxylate or unsaturated glycidyl ether, and ethylenically unsaturated ester compound.

Examples of ethylenically unsaturated ester compounds giving the constituent (c) include vinyl carboxylates, such as vinyl acetate and vinyl propionate, and unsaturated  $\alpha,\beta$ -alkyl carboxylates, such as methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate, and butyl methacrylate. Vinyl acetate, methyl acrylate, and ethyl acrylate are especially preferable.

Examples of the epoxy group-containing ethylene copolymer of component (B) applied to the invention include ethylene-glycidyl methacrylate-methyl methacrylate terpolymer, ethylene-glycidyl methacrylate-methyl acrylate terpolymer, ethylene-glycidyl methacrylate-ethyl acrylate terpolymer, and ethylene-glycidyl methacrylate-vinyl acetate terpolymer.

The epoxy group-containing ethylene copolymer included as the component (B) in the liquid crystal polyester resin composition of the invention includes:

- (a) 50 through 96.5 percent by weight of an ethylene unit;
- (b) 0.5 through 30 percent by weight of an unsaturated glycidyl carboxylate unit or an unsaturated glycidyl ether unit; and
- (c) 3 through 40 percent by weight of an ethylenically unsaturated ester compound unit.

The content of the ethylene unit (a) greater than 96.5 percent by weight undesirably lowers the impact resistance whereas the same less than 50 percent by weight results in a poor rigidity.

The content of the unsaturated glycidyl carboxylate unit or unsaturated glycidyl ether unit (b) greater than 30 percent by weight undesirably lowers the rigidity whereas the same less than 0.5 percent by weight gives a poor impact resistance.

The content of the ethylenically unsaturated ester compound unit greater than 40 percent by weight undesirably lowers the rigidity whereas the same less than 3 percent by weight causes a poor impact resistance.

The melt index (hereinafter may be referred to as MFR: measured at 190 °C under a load of 2.16 kg in conformity with JIS K6760) of the epoxy group-containing ethylene copolymer is in a range of 0.5 through 100 g/10 minutes or more preferably in a range of 2 through 50 g/10 minutes. The melt index greater than 100 g/10 minutes results in poor mechanical properties of the resulting resin composition while that less than 0.5 g/10 minutes lowers the compatibility with the liquid crystal polyester of component (A).

The epoxy group-containing ethylene copolymer of component (B) applied to the invention has stiffness modulus in a range of 10 through 1300 kg/cm<sup>2</sup> or more preferably in a range of 20 through 1100 kg/cm<sup>2</sup>. The stiffness modulus out of the above range may result in insufficient processabilities and mechanical properties of the resulting resin composition.

The epoxy group-containing ethylene copolymer is prepared by copolymerizing an unsaturated epoxy compound and ethylene with a radical polymerization initiator at 500 through 4000 atm and 100 through 300 °C in the presence of or absence of an appropriate solvent and a chain transfer agent. Alternatively, a mixture of polyethylene and an unsaturated epoxy compound may be fused and graft-copolymerized in an extruder in the presence of a radical polymerization initiator.

The content of the component (A) included in the thermoplastic resin composition of the invention is 55.0 through 99.9 percent by weight or more preferably 65.0 through 99.0 percent by weight while the content of the component (B) is within a range of 0.1 through 45.0 percent by weight or more preferably in a range of 1.0 through 35.0 percent by weight.

The content of the component (A) less than 55.0 percent by weight lowers the heat resistance of the resulting resin composition, and the same greater than 99.9 percent by weight does not sufficiently improves the anisotropy and increases the cost.

The liquid crystal polyester resin composition of the invention may be manufactured by any known method. A typical method mixes the component (A) with the component (B) respectively dissolved in a

solvent, and collects the resulting resin composition by evaporating the solvent or precipitating the resin composition. An industrially preferable method is to knead the components under the molten state. Known kneading apparatus including single screw extruders, twin-screw extruders, and various kneaders are applicable to the kneading process. Especially, biaxial high-speed kneaders are preferably applied.

5 For the kneading process, the temperature in the cylinder of the kneading machine is set in a range of 200 through 360 °C or more specifically in a range of 230 through 350 °C.

Each component may be pre-mixed to the homogeneous state with a tumbling mixer or Henschel mixer. However, the components may be separately introduced quantitatively into a kneader without pre-mixing.

10 According to a typical method, the kneaded resin composition is formed to a predetermined shape by injection molding, extrusion molding, or another known molding process. Alternatively, molded articles may be obtained directly by dry blending the components and subsequently melt processing them by injection molding or extrusion molding.

An inorganic filler may be added to the liquid crystal polyester resin composition of the invention according to the requirements. Examples of the applicable inorganic filler include calcium carbonate, talc, 15 clay, silica, magnesium carbonate, barium sulfate, titanium oxide, alumina, plaster, glass flakes, glass fibers, carbon fibers, alumina fibers, silica alumina fibers, aluminum borate whiskers, and potassium titanate fibers.

Various additives may also be added to the liquid crystal polyester resin composition of the invention according to the requirements in the preparation process or the subsequent melt processing process. Such 20 additives include organic fillers, antioxidants, heat stabilizers, light stabilizers, flame retardants, lubricants, antistatic agents, inorganic or organic colorants, rust preventives, crosslinking agents, foaming agents, fluorescent agents, surface smoothing agents, surface gloss improvers, and mold release agents such as fluoropolymers.

Films formed from the liquid crystal polyester resin composition of the invention have excellent heat 25 resistance and gas barrier properties.

It is generally preferable that the flow temperature of the liquid crystal polyester resin composition is higher than the flow temperature of the liquid crystal polyester of component (A). The resin composition having the flow temperature lower than that of the liquid crystal polyester may result in poor mechanical properties.

30 The liquid crystal polyester resin composition has a melt viscosity ratio (melt viscosity 2 / melt viscosity 1) of 0.1 through 0.7 being measured at a shear rate of either 100 sec<sup>-1</sup> or 1000 sec<sup>-1</sup>, said melt viscosity 1 being measured at a flow temperature and said melt viscosity 2 being measured at a temperature of 20 °C higher than said flow temperature.

For film formation, preferable range of the melt viscosity ratio of the liquid crystal polyester resin 35 composition is between 0.1 and 0.7. The more preferable range of the melt viscosity ratio of the liquid crystal polyester resin composition is between 0.1 and 0.5. The melt viscosity ratio out of the above range lowers the film forming properties or results in the poor anisotropy and tensile strength of the resulting films.

The flow temperature initiates formation of an anisotropic melt phase and gives a melt viscosity of 40 48,000 poise when a resin heated at a rate of 4 °C/minute is extruded from a nozzle having an inner diameter of 1mm and length of 10 mm under a load of 100 Kgf/cm<sup>2</sup>.

The liquid crystal polyester resin composition of the invention is molded to films according to a known method.

The liquid crystal polyester resin composition of the invention has excellent vibration-damping prop- 45 erties, solder heat resistance, thin-wall properties, and film-forming properties as well as gives favorable gas barrier properties to the molded films, though the reasons for such improvement are not clearly elucidated. It is, however, assumed that chemical reaction of the liquid crystal polyester with the epoxy group-containing ethylene copolymer improves the compatibility of the liquid crystal polyester with the epoxy group-containing ethylene copolymer.

50 Fig. 1 shows a test piece applied to measurement of strengths at a welded portion and at a non-welded portion.

## EXAMPLES

## (1) Measurement of Properties

5 Flow temperature.

The flow temperature was measured with a flow tester CFT-500 (manufactured by Shimadzu Corp). The flow temperature was measured as a temperature giving a melt viscosity of 48,000 poise when a resin heated at a rate of 4 °C/minute was extruded from a nozzle having an inner diameter of 1mm and length of 10 mm under a load of 100 Kg/cm<sup>2</sup>.

Melt Viscosity:

The melt viscosity was measured at shear rates of 100 sec<sup>-1</sup> and 1000 sec<sup>-1</sup> with Capillograph 1B (diameter of die: 0.5 mm) manufactured by Toyo Seiki Co., Ltd.

Tensile strength & Temperature of deflection under load (TDUL):

ASTM No. 4 tensile dumbbells and TDUL test samples (127 mm in length x 12.7 mm in width x 6.4 mm in thickness) were prepared, and the tensile strength and TDUL (under the load of 18.6 kg) were measured in conformity with ASTM (American Society for Testing and Materials) D638 and ASTM D648, respectively.

Izod impact strength:

The Izod impact strength was measured without notches for test samples (6.4 mm in thickness) at the ambient temperature and -40 °C according to JIS K7110.

Vibration-damping pproperties:

The viscoelasticity was measured for each injection molded article in an atmosphere of nitrogen at a heating rate of 5 °C/min with a viscoelasticity measurement device DMA (manufactured by du Pont) according to the resonant frequency measurement process. Those having the high loss tangent (tanδ) were determined to have preferable vibration-damping properties.

35 Thin-wall properties:

Each composition was injection molded to dumbbell samples at a predetermined molding temperature and a predetermined die temperature with a die (wall thickness: 0.5 mm, length: 75 mm, width of neck: 5 mm). The tensile test was performed for the dumbbell samples to determine the elongation and tensile strength.

Thin-wall flow length:

Each composition was injected into a rectangular four-cavity mold (wall thickness: 0.3 mm, length: 46 mm, width: 5 mm) at 340 °C under a predetermined injection condition. The flow length of the composition along a longitudinal direction of each cavity was measured for the four cavities, and the mean value was calculated as the thin-wall flow length.

Strength at welded portion & Strength at non-welded portion:

Test pieces shown in Fig. 1 were formed from the respective compositions. Each test piece had the thickness of 3 mm, the outer diameter of 64 mm, and the inner diameter of 38 mm. A welded portion 2 (64 x 13 mm) including a weld line 1 (filled with slant lines in Fig. 1) was cut from the test piece, and the flexural strength was measured under the condition of the inter-span distance of 40 mm and the flexural rate of 2 mm/min.

A non-welded portion (64 x 13 mm) was also cut from the test piece and measured for the flexural strength.

Solder heat resistance:

JIS No. 1(1/2) Dumbbells of 0.8 mm in thickness were prepared and immersed in a solder bath containing 60% tin and 40% lead and heated to 260 °C. After the immersion at the fixed temperature for 60 seconds, the dumbbells were taken out of the solder bath and observed with the naked eye. Similar experiments were carried out as the temperature of the solder bath was increased by 10 °C every time. The maximum temperature of the solder bath which did not cause foaming or deformation of the test pieces was determined. For example, when the test piece starts foaming or deformation at 310 °C, the solder heat resistance is determined to be 300 °C.

Appearance of film:

Films formed from the respective compositions were observed with the naked eye and evaluated according to the criteria below:

- : preferable appearance without any segregation or mottle; and
- △: segregation or mottle observed.

Oxygen transmission rate of film:

The oxygen transmission rate was measured with oxygen gas at the temperature of 20 °C in conformity with the differential pressure method of JIS K7126.

Water vapor transmission rate of film:

The water vapor transmission rate was measured at the temperature of 40 °C and the relative humidity of 90% in conformity with the cup method of JIS Z0208.

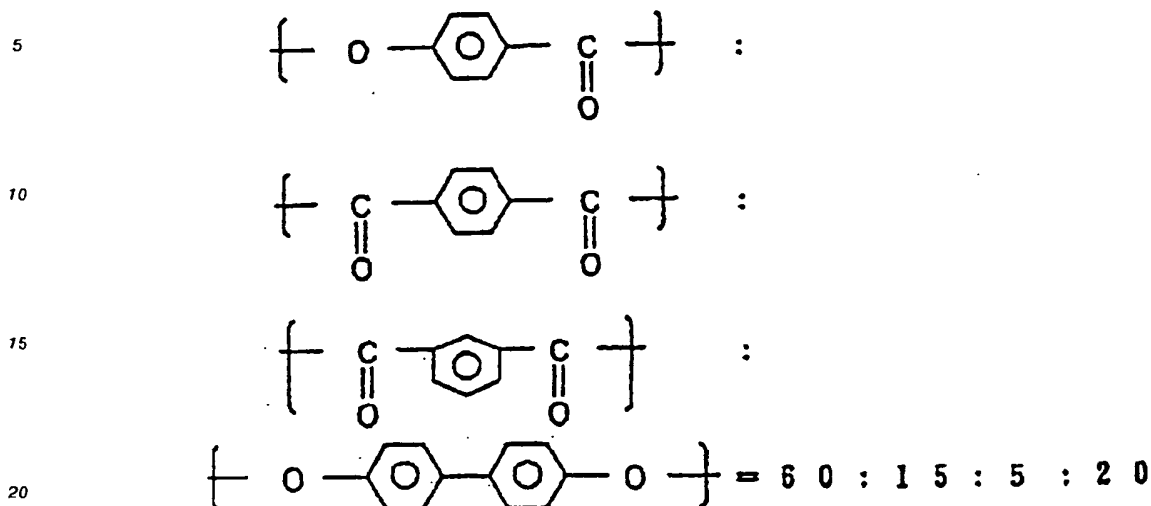
The oxygen transmission rate and the water vapor transmission rate were converted to the film thickness of 25 μm.

## (2) Liquid crystal polyester of component (A)

(i) A mixture containing 10.8 kg (60 mole) of p-acetoxybenzoic acid, 49 kg (15 mole) of terephthalic acid, 0.83 kg (5 mole) of isophthalic acid, and 5.45 kg (20.2 mole) of 4,4'-diacetoxydiphenyl was placed in a polymerization tank equipped with a comb-type agitator and stirred in an atmosphere of nitrogen upon continued heating to 330 °C. The mixture was polymerized at 330 °C for one hour with vigorous stirring while acetic acid produced as a by-product was continuously removed. The system was gradually cooled to 200 °C, at which the polymer obtained was taken out of the system.

The polymer obtained was ground to particles of not greater than 2.5 mm in diameter with a hammer mill (manufactured by Hosokawa Micron Co., Ltd). The polymer particles were treated in an atmosphere of nitrogen at 280 °C in a rotary kiln for three hours, so that granules of aromatic polyester (flow temperature: 324 °C) consisting of repeat units shown below were obtained. The liquid crystal polyester thus obtained was hereinafter referred to as A-1. The polymer showed optical anisotropy under the pressurizing condition at temperatures of not less than 340 °C, and had the inherent viscosity  $\eta_{inh}$  of 2.5. The ratio of the repeat units of the polyester A-1 was given as:

## [Chemical Formula 18]

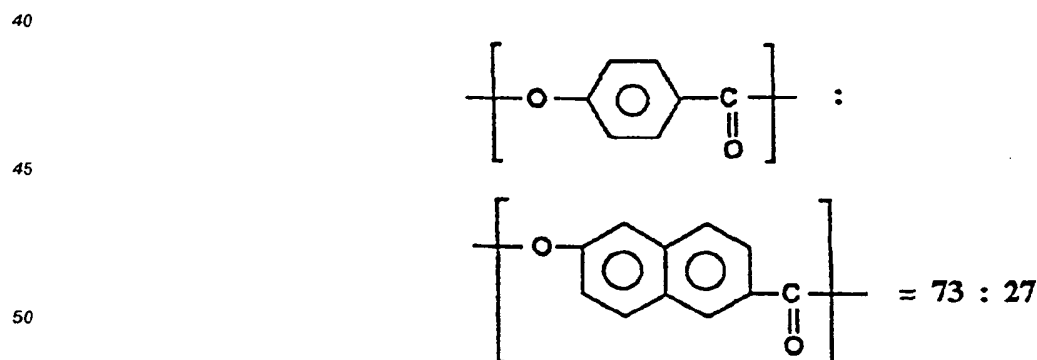


(ii) A mixture containing 16.6 kg (12.1 mole) of p-hydroxybenzoic acid, 8.4 kg (4.5 mole) of 6-hydroxy-2-naphthoic acid, and 18.6 kg (18.2 mole) of acetic anhydride was placed in a polymerization tank equipped with a comb-type agitator and stirred in an atmosphere of nitrogen upon continued heating to 320 °C. The mixture was polymerized at 320 °C for one hour and under a reduced pressure of 2.0 torr at 320 °C for another one hour with vigorous stirring while acetic acid produced as a by-product was continuously removed from the system. The system was gradually cooled to 180 °C, at which the polymer obtained was taken out of the system.

The polymer obtained was ground to particles in the same manner as the process (i) and treated in an atmosphere of nitrogen at 240 °C in a rotary kiln for five hours, so that granules of aromatic polyester (flow temperature: 270 °C) consisting of repeat units shown below were obtained. The liquid crystal polyester thus obtained was hereinafter referred to as A-2. The polymer showed optical anisotropy under the pressurizing condition at temperatures of not less than 280 °C, and had the inherent viscosity  $\eta_{inh}$  of 5.1.

The ratio of the repeat units of the polyester A-2 was given as:

## [Chemical Formula 19]



### 55 (3) Epoxy group-containing ethylene copolymer of component (B)

The following copolymers were used for the epoxy group-containing ethylene copolymer of component (B):

B-1: trade name Bondfast 7L manufactured by Sumitomo Chemical Co., Ltd.  
 Composition: ethylene / glycidyl methacrylate / methyl acrylate = 67 / 3 / 30  
 MFR (measured at 190 °C under the load of 2.16 kg) = 9 g/10 minutes; stiffness modulus = 60 kg/cm<sup>2</sup>

5 B-2: trade name Bondfast 2C manufactured by Sumitomo Chemical Co., Ltd.  
 Composition: ethylene / glycidyl methacrylate = 94 / 6 MFR (measured at 190 °C under the load of  
 2.16 kg) = 3 g/10 minutes; stiffness modulus = 1,000 kg/cm<sup>2</sup>

B-3: trade name Bondfast 20B manufactured by Sumitomo Chemical Co., Ltd.  
 Composition: ethylene / glycidyl methacrylate / vinyl acetate = 83 / 12 / 5  
 MFR (measured at 190 °C under the load of 2.16 kg) = 20 g/10 minutes; stiffness modulus = 430 kg/cm<sup>2</sup>

10 Examples 1 through 5, References 1 & 2

The respective components and a stabilizer were blended with a Henschel mixer according to the  
 compositions shown in Tables 1 and 3. Each composition was kneaded at the cylinder temperature of  
 15 327 °C with a twin-screw extruder PCM-30 (manufactured by Ikegai Tekko Co., Ltd). The kneaded  
 composition was injection molded to an article with an injection molding device PS40E5ASE (manufactured  
 by Nissei Resin Industries Co., Ltd.) at the molding temperature of 347 °C and the die temperature of 80 °C.  
 The properties of each molded article were measured, and the results of measurement are shown in Tables  
 1 and 3.

20 Each composition obtained as above was also extrusion molded to a film by a single screw extruder  
 VS20-20 (manufactured by Tanabe Plastics Co., Ltd.) with a T-die. The composition was extruded from the  
 T-die having the slit width of 10 cm and the slit interval of 0.7 mm under the conditions of the cylinder  
 temperature of 350 through 360 °C and the screw speed of 80 rpm. The film wound up at the rate of 4  
 m/min had the thickness of 20 through 50 μm. The properties of each film were measured, and the results  
 25 of measurement are shown in Table 3.

Example 6, References 3 & 4

30 The respective components and a stabilizer were blended with a Henschel mixer according to the  
 compositions shown in Tables 2 and 4. Each composition was kneaded at the cylinder temperature of  
 257 °C with a twin-screw extruder PCM-30 (manufactured by Ikegai Tekko Co., Ltd). The kneaded  
 composition was injection molded to an object with an injection molding device PS40E5ASE (manufactured  
 by Nissei Resin Industries Co., Ltd.) at the molding temperature of 258 °C and the die temperature of 60 °C.  
 The properties of each molded object were measured, and the results of measurement are shown in Tables  
 35 2 and 4.

Each composition obtained as above was extrusion molded to a film in the same manner as above  
 except that the temperature of cylinder in the extruder was set in a range of 280 through 310 °C. The  
 properties of each film were measured, and the results of measurement are shown in Table 4.

40 The liquid crystal polyester resin composition of the invention is manufactured at low cost and has  
 favorable solder heat resistance, film-forming properties, and gas barrier properties as well as improved  
 weld strength, vibration-damping properties, and thin-wall properties. The liquid crystal polyester resin  
 composition is preferably applicable to various molded articles, such as sheets, tubes, films, fibers,  
 laminates, and coating materials, prepared by injection molding or extrusion molding.

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Table 1

	Composition			Flow temperature (FT)	Melt viscosity 1		Melt viscosity 2		Melt viscosity ratio	
	Component A	Component B	Another component		Measured at FT		Measured at FT + 20°C		$\frac{\text{Melt viscosity 2}}{\text{Melt viscosity 1}}$	
					100 sec <sup>-1</sup>	1000 sec <sup>-1</sup>	100 sec <sup>-1</sup>	1000 sec <sup>-1</sup>	100 sec <sup>-1</sup>	1000 sec <sup>-1</sup>
					Poise		Poise			
Example 1	(A-1) 98	(B-1) 2	0	321	48000	8200	4900	1000	0.102	0.122
Example 2	(A-1) 95	(B-1) 5	0	321	47000	8400	5500	1200	0.111	0.143
Example 3	(A-1) 90	(B-1) 10	0	322	44000	7800	6300	1400	0.143	0.179
Example 4	(A-1) 80	(B-1) 20	0	326	42000	7400	7600	1800	0.181	0.250
Example 5	(A-1) 70	(B-1) 30	0	332	37000	6800	9500	2150	0.257	0.316
Reference 1	(A-1) 100	0	0	320	48000	8200	3000	700	0.063	0.085
Reference 2	(A-1) 80	0	20 **	245	23000	4200	18000	3400	0.783	0.810

\*1 Low-density Polyethylene, Sumikathene F-101 (Registered Trademark); Manufactured by Sumitomo Chemical Co., Ltd.  
( Stiffness modulus = 2300 kg/cm<sup>2</sup> )



Table 2

	Composition			Flow temperature (°C)	Melt viscosity 1		Melt viscosity 2		Melt viscosity ratio
	Component A	Component B	Another component		Measured at FT		Measured at FT + 20°C		
					100 sec <sup>-1</sup>	1000 sec <sup>-1</sup>	100 sec <sup>-1</sup>	1000 sec <sup>-1</sup>	
Percent by weight									
Reference 3	(A-2) 92	(B-2) 8	0	265	42000	7600	8500	1800	0.237
	(A-2) 80	(B-3) 20	0		41000	7200	13000	3000	
Reference 4	(A-2) 100	0	0	263	56000	9200	4900	1500	0.163

Table 3

	Properties													
	Tensile test		TDUL	Izod impact strength		Tan $\delta$		Thin-wall properties			Strength at non-welded portion	Strength at welded portion	Solder heat resistance	
								Elongation	Tensile strength at break	Thin-wall flow length				
	(%)	(kg/cm <sup>2</sup> )	( °C )	(kg·cm/cm)	25°C	150 °C	(%)				(kg/cm <sup>2</sup> )	(340°C ,mm)	(kg/cm <sup>2</sup> )	(°C)
	Example 1	7.5	1700	259	83	27	0.08	0.06	9.0	3040	177	740	250	300
	Example 2	7.8	1730	254	86	29	0.08	0.07	9.4	3090	184	730	290	290
Example 3	10.1	1990	243	No break-age	33	0.07	0.09	9.1	3000	191	700	320	290	
Example 4	10.4	1360	238	56	35	0.11	0.12	8.6	2350	150	610	310	290	
Example 5	9.4	990	215	43	29	0.12	0.14	8.2	1760	103	520	300	280	
Reference 1	5.2	1620	265	70	30	0.04	0.03	4.0	3060	162	780	200	300	
Reference 2	1.2	790	201	7	2	0.03	0.02	2.1	1040	85	460	250	260	

Table 3  
(Continued)

	Film properties		
	Appearance of film	Water vapor transmission rate (g/m <sup>2</sup> ·24hr·atm)	Oxygen transmission rate (cc/m <sup>2</sup> ·24hr·atm)
Example 1	Δ	0.3	0.3
Example 2	○	0.4	0.3
Example 3	○	0.3	0.2
Example 4	○	0.4	0.4
Example 5	○	0.5	0.4
Reference 1	No film formed	-	-
Reference 2	No film formed	-	-

Table 4

	Properties									
	Tensile test		TDUL	Izod impact strength		Tan $\delta$		Thin-wall properties		Strength at non-welded portion
	Elon-gation	Tensile strength at break		r. t.	-40°C	25°C	150 °C	Elon-gation	Tensile strength at break	Strength at welded portion
	(%)	(kg/cm <sup>2</sup> )	( °C )	(kg·cm/cm)				(%)	(kg/cm <sup>2</sup> )	(kg/cm <sup>2</sup> )
Reference 3	13.7	1990	180	No break-age	15	0.08	0.09	12.4	1830	780
Example 6	12.8	1280	158	86	32	0.10	0.11	10.8	1770	670
Reference 4	11.5	1740	183	71	31	0.02	0.02	6.9	1970	920
										Cracking (not measured)

(Continued)

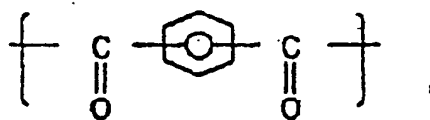
Table 4	Film properties				
	Appearance of film	Water vapor transmission rate (g/m <sup>2</sup> ·24hr·atm)	Oxygen transmission rate (cc/m <sup>2</sup> ·24hr·atm)		
	Reference 3	△	0.4	0.3	
	Example 6	○	0.4	0.4	
	Reference 4	No film formed	-	-	

### Claims

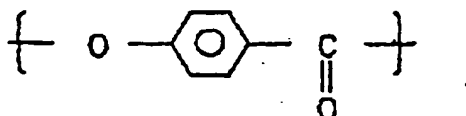
1. A liquid crystal polyester resin composition comprising 55.0 through 99.9 percent by weight of a liquid crystal polyester as a component (A) and 0.1 through 45.0 percent by weight of an epoxy group-containing ethylene copolymer as a component (B),  
said component (B) comprising:
  - (a) 50 through 96.5 percent by weight of an ethylene unit;
  - (b) 0.5 through 30 percent by weight of an unsaturated glycidyl carboxylate unit or an unsaturated glycidyl ether unit; and
  - (c) 3 through 40 percent by weight of an ethylenically unsaturated ester compound unit.
2. A liquid crystal polyester resin composition according to claim 1, wherein said liquid crystal polyester of component (A) is obtained through a reaction of an aromatic dicarboxylic acid, an aromatic diol, and an aromatic hydroxycarboxylic acid.
3. A liquid crystal polyester resin composition according to claim 1, wherein said liquid crystal polyester of component (A) is obtained through a reaction of different aromatic hydroxycarboxylic acids.
4. A liquid crystal polyester resin composition according to claim 1 or 2, wherein said liquid crystal polyester of component (A) comprises repeat units given as Chemical Formulae 1 below:

## [Chemical Formulae 1]

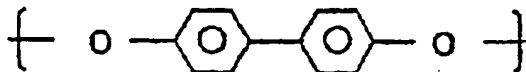
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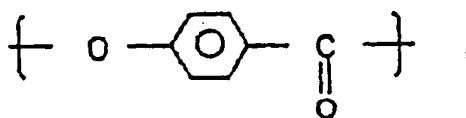


5. A liquid crystal polyester resin composition according to claim 1 or 3, wherein said liquid crystal polyester of component (A) comprises repeat units given as Chemical Formulae 2 below:

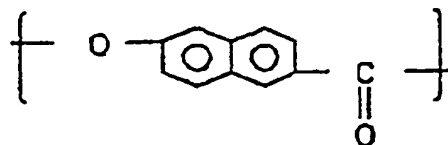
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## [Chemical Formulae 2]

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- 35 6. A liquid crystal polyester resin composition according to any of claims 1 to 5, wherein said epoxy group-containing ethylene copolymer of component (B) has a stiffness modulus in a range of 10 through 1,300 kg/cm<sup>2</sup>.

- 40 7. A liquid crystal polyester resin composition according to any of claims 1 to 6, wherein the melt viscosity ratio (melt viscosity 2 / melt viscosity 1) of said liquid crystal polyester resin composition being measured at a shear rate of either 100 sec<sup>-1</sup> or 1000 sec<sup>-1</sup> is in a range of 0.1 through 0.7,

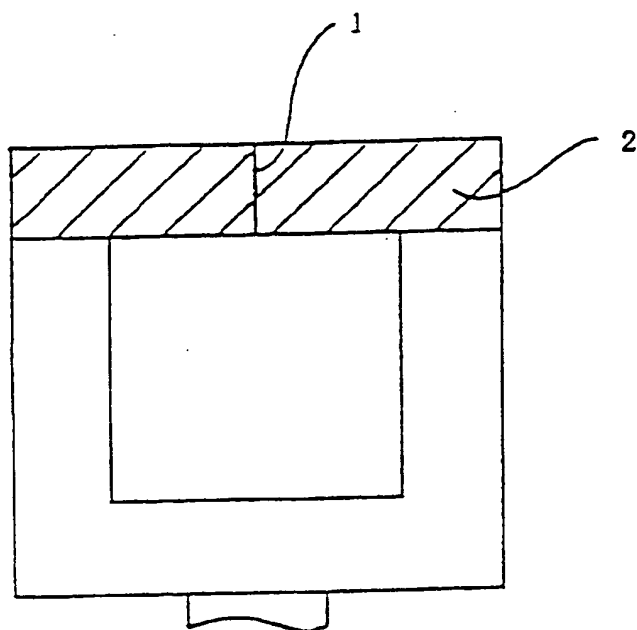
said melt viscosity 1 being measured at a flow temperature and said melt viscosity 2 being measured at a temperature of 20 °C higher than said flow temperature.

- 45 8. A liquid crystal polyester resin composition according to any of claims 1 to 7, wherein said liquid crystal polyester of component (A) has an inherent viscosity  $\eta_{inh}$  of 1.0 through 8.0.

- 50 9. A liquid crystal polyester resin composition according to any of claims 1 to 8, wherein the flow temperature of said liquid crystal polyester resin composition is higher than a flow temperature of said liquid crystal polyester of component (A).

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Figure 1









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(54) **Liquid crystal polyester resin composition.**

(57) The present invention provides a liquid crystal polyester resin composition, which is manufactured at low cost and has favorable gas barrier properties and improved impact resistance, vibration-damping properties, thin-wall properties (mechanical properties of thin-wall molded articles), and film-forming properties, while maintaining excellent heat resistance and mechanical properties of a liquid crystal polyester. A liquid crystal polyester resin composition of the invention includes 55.0 through 99.9 percent by weight of a liquid crystal polyester as a component (A) and 0.1 through 45.0 percent by weight of an epoxy group-containing ethylene copolymer as a component (B), wherein the component (B) includes: (a) 50 through 96.5 percent by weight of an ethylene unit; (b) 0.5 through 30 percent by weight of an unsaturated glycidyl carboxylate unit or an unsaturated glycidyl ether unit; and

(c) 3 through 40 percent by weight of an ethylenically unsaturated ester compound unit.

**EP 0 672 721 A3**



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## EUROPEAN SEARCH REPORT

Application Number  
EP 95 10 3761

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
P,X	EP-A-0 595 082 (BAYER AG) * claims 1,2,4; example 4 * * page 2, line 56 - page 5, line 43 * ---	1-5	C08L67/00 C09K19/54 C09K19/38 /(C08L67/00, 23:08)
X	EP-A-0 380 112 (KAWASAKI STEEL CORP.) * claims 1,2; example 19 * * page 2, line 1 - line 28 * * page 3, line 20 - page 5, line 57 * ---	1-5	
D,X	US-A-5 216 073 (M.I. HAIDER ET AL.) * claims 1-8; example 1 * * column 3, line 22 - column 4, line 17 * ---	1-5	
X	EP-A-0 472 898 (NIPPON PETROCHEMICALS COMP., LTD.) * claims 1,8; example 18 * ---	1	
X	CHEMICAL ABSTRACTS, vol. 117, no. 4, 27 July 1992, Columbus, Ohio, US; abstract no. 28004, * abstract * & JP-A-4 028 743 (SUMITOMO CHEMICAL COMP., LTD.) 31 January 1992 ---	1,2	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
X	CHEMICAL ABSTRACTS, vol. 119, no. 20, 15 November 1993, Columbus, Ohio, US; abstract no. 205053, * abstract * & JP-A-5 078 556 (MITSUBISHI CHEM. IND.) 30 March 1993 ---	1,2	C08L
A	EP-A-0 247 465 (BASF AG) * claim 1; example 3 * * page 5, line 21 - line 31 * * page 6, line 30 - page 7, line 30 * --- -/--	1	
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 9 August 1995	Examiner Krische, D
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons * : member of the same patent family, corresponding document			

EPO FORM 1503 (03.92) (P0404)



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## EUROPEAN SEARCH REPORT

Application Number  
EP 95 10 3761

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	CHEMICAL ABSTRACTS, vol. 116, no. 6, 10 February 1992, Columbus, Ohio, US; abstract no. 42639, * abstract * & JP-A-3 220 260 (POLYPLASTICS CO., LTD.) 27 September 1991 ---	1	
A	DATABASE WPI Week 8826, Derwent Publications Ltd., London, GB; AN 88-177764 & JP-A-63 113 056 (SUMITOMO CHEMICAL IND. KK) 18 May 1988 * abstract * -----	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 9 August 1995	Examiner Krische, D
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document			

EPO FORM 150 (02.92) (P0401)

